

Phase-field-crystal modeling of the (2×1) - (1×1) phase-transitions of Si(001) and Ge(001) surfaces

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Abstract. We propose a two-dimensional phase-field-crystal model for the (2×1) - (1×1) phase transitions of Si(001) and Ge(001) surfaces. The dimerization in the 2×1 phase is described with a phase-field-crystal variable which is determined by solving an evolution equation derived from the free energy. Simulated periodic arrays of dimerization variable is consistent with scanning-tunnelling-microscopy images of the two dimerized surfaces. Calculated temperature dependence of the dimerization parameter indicates that normal dimers and broken ones coexist between the temperatures describing the characteristic temperature width of the phase-transition, T_L and T_H , and a first-order phase transition takes place at a temperature between them. The dimerization over the whole temperature is determined. These results are in agreement with experiment. This phase-field-crystal approach is applicable to phase-transitions of other reconstructed surface phases, especially semiconductor $n\times 1$ reconstructed surface phases.

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1. Introduction

Semiconductor surfaces are of huge importance especially in the modern era of nanoscience and nanotechnology. Usually, a bulk terminated surface (1×1) is unstable, will undergo a surface reconstruction and become a stable reconstructed surface phase ($m \times n$) [1, 2, 3]. Most of reconstructed surfaces transit to some 1×1 structures at elevated temperatures. The Si(001) and Ge(001) reconstructed surfaces have been extensively studied because they are closely relevant to the modern computer technology [4, 5]. For both of them, the reconstruction is realized through the forming of regular arrays of dimers in the top layer (2×1 or dimerized phase), which has been confirmed by scanning-tunnelling-microscopy (STM) experiment [1, 4, 5]. It was shown experimentally [6, 7] that when heated to certain temperatures, the 2×1 reconstructed surfaces will transit to 1×1 structures. There were some first-principles calculations for the local atomic configurations of the 2×1 surfaces [8], but it is controversial even for the essence of the phase transitions [6, 7]. Considering that a structural phase means an averaging of local atomic structures over large enough scales, the reconstructed surface phases need further clarification and the essential physics of the phase transitions are still unknown. A theory that can elucidate the issues is highly desirable.

Phase-field method is a reliable approach to modeling and simulating structural phases and dynamical phase transitions [9, 10]. It has been applied to various fields such as spiral surface growth [11], dendritic growth [12], alloy solidification [13], crystal nucleation [14], step-flow growth [15, 16], epitaxial island growth [17, 18, 19], and surface phase transition dynamics [20]. Recently, a phase-field-crystal approach was proposed to model the internal spatial structures of a given phase [21], and periodic lattices was obtained by solving evolution equations derived from the free energies. This powerful approach has been successfully used for natural modeling of elastic interactions [22] and binary alloy solidification [23].

In this paper we propose a phase-field-crystal model for the Si(001) and Ge(001) dimerized surface phases and their phase transitions. We use a two-dimensional (2D) phase-field-crystal variable to describe the dimerization of atoms in the top layer, and determine the variable by solving an evolution equation derived from the free energy. Our simulated morphology of periodic arrays of the dimerization variable is in good agreement with large-scale STM images of the Si(001) and Ge(001) surfaces in high-quality samples [2, 3, 4, 5]. Furthermore, we derive the temperature dependence of the dimerization parameter, and show that normal dimers and broken ones coexist between two characteristic temperatures, T_L and T_H , and a first-order phase transition takes place at a phase-transition temperature T_c in between T_L and T_H . These are in agreement with experiment [6, 7]. This phase-field-crystal approach can be applied to other reconstructed surface phases and their phase-transition dynamics.

The remaining part of this paper is organized as follows. In next section we shall present our phase-field-crystal modeling for the 2×1 phase and its phase transition dynamics during transiting to the 1×1 phase. In section III we shall present our main

simulated results. In section IV we shall apply the model and the simulated results to the (2×1) - (1×1) phase transitions of Si(001) and Ge(001) dimerized surfaces. Finally, we shall give our conclusion in section V.

2. Phase-field-crystal modeling

There are two kinds of the (001) surfaces, type- S_A and type- S_B , for both Si and Ge. They appear alternately in the vertical direction, but do not exist in the same layer in high-quality samples, although they can be changed into each other by a 90° rotation [4, 5]. Because the dimerization takes place only in the top layer, it is reasonable to describe both of the Si(001) and Ge(001) dimerized surface phases by a 2D model. We neglect the buckling of dimers without losing main physics because we are mainly interested in their high-temperature phase transitions to corresponding 1×1 phases. We show the atomic configurations and corresponding phase-field-crystal modeling in Fig. 1. We use $\vec{r} = (\bar{x}, \bar{y})$ for a 2D point, where \bar{x} describes the coordinate in the dimerization direction or the horizontal direction and \bar{y} in the other direction. The key order parameter is the dimerization-induced change of the bond length, Δb , in the horizontal or \bar{x} direction because there is no dimerization in the other direction [6, 7]. Phase-field-crystal variable $\phi(\bar{x}, \bar{y})$ is periodic in the \bar{x} direction and uniform in the other direction. Along the \bar{x} direction, $\phi(\bar{x}, \bar{y})$ reaches the maximum, ϕ_{\max} , at the center of the dimer and the minimum, $-\phi_{\max}$, at the middle point of the two nearest dimers with the same \bar{y} . This model is consistent with STM images of regular arrays of dimer chains in high-quality Si(001) and Ge(001) dimerized surfaces [4, 5, 6, 7]. The average value of $\phi(\bar{x}, \bar{y})$ over \vec{r} , $\bar{\phi}$, is set to zero for the dimerized surfaces. The variable $\phi(\bar{x}, \bar{y})$ for the dimerized surfaces is normalized so as to make the integration of $|\phi(\bar{x}, \bar{y})|$ over the 2D unit cell equal $2\Delta b$ because there are two top-layer atoms in the 2D unit cell. The variable $\phi(\bar{x}, \bar{y})$ is identical to zero for the undimerized surfaces. These are enough for the following phase-field simulation, but, with all these in our mind, we can imagine that the morphology of the phase-field variable $\phi(\bar{x}, \bar{y})$ can be described approximately by a simple function $\frac{\pi\Delta b}{c^2} \cos(\pi\bar{x}/c)$, where c is the lattice constant of the undimerized 2D unit cell and the center of the dimer is taken as the zero point of \bar{x} .

The free energy of $\phi(\bar{x}, \bar{y})$ can be written as

$$\mathcal{F} = \lambda \int_{\Omega} d\vec{r} \left\{ \frac{1}{2} \phi \left[A + \left(q_0^2 + \frac{\partial^2}{\partial \bar{x}^2} \right)^2 \right] \phi - u_4 \frac{\phi^4}{4} + u_6 \frac{\phi^6}{6} \right\}, \quad (1)$$

where the A is defined by $A = a(T - T_L)$, and the parameters λ , u_4 , u_6 , and a are positive constants. q_0 is defined as $2\pi/\bar{c}_0$ and \bar{c}_0 has the meaning of lattice constant if periodic solution is obtained. The operator $G = (q_0^2 + \frac{\partial^2}{\partial \bar{x}^2})^2$ is constructed by fitting to the dimerization structure [21]. The u_4 and u_6 terms, as usual, are used to describe the first-order phase transitions in the Si(001) and Ge(001) surfaces. The bilinear term is used to describe the effect of temperature and dimerization structure. The parameter u_6 can be set to 1 by redefining the phase-field-crystal variables without losing any physics.

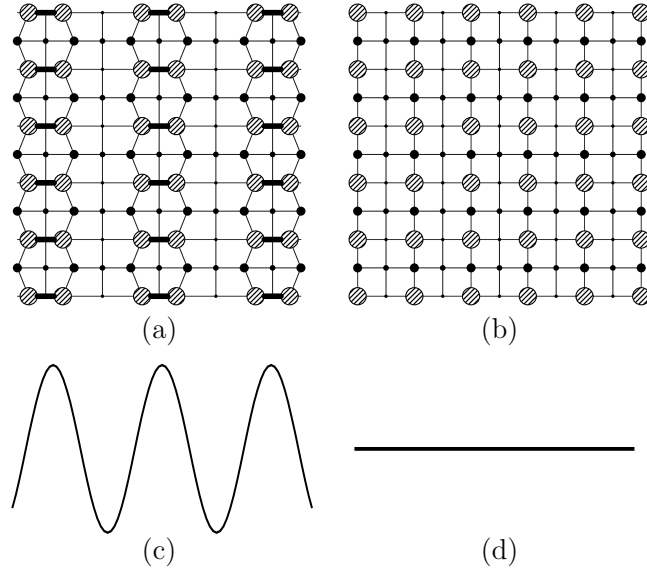


Figure 1. The phase-field-crystal modeling of the Si(001) and Ge(001) dimerized phases. (a) shows atomic models of the dimerized (001) surfaces and (b) that of bulk-terminated (001) ones. The dimerization happens only in the horizontal (or \bar{x}) direction. The gray circle is the atom in the top layer, the bigger black dot in the second layer, and the smaller black dot in the third layer. The curve (c) is schematic phase-field-crystal ϕ description of the dimerization-induced atomic density change with respect to that without dimerization (d).

The evolution equation of ϕ is a time-dependent Cahn-Hilliard (CH) equation [24]

$$\frac{\partial \phi}{\partial t} = \Gamma \nabla_r^2 \frac{\delta \mathcal{F}}{\delta \phi} + \eta, \quad (2)$$

where η is a Gaussian random variable whose average value is set to zero. The first term on the right side describes the diffusion of the phase-field variable. Using the dimensionless phase-field variable ψ , dimensionless coordinates \vec{x} , and dimensionless time τ defined by [21]

$$\vec{x} = (x, y) = q_0 \vec{r}, \quad \psi = \frac{\sqrt[4]{u_6}}{q_0} \phi, \quad \tau = \lambda \Gamma q_0^6 t, \quad (3)$$

we express the free energy (1) and the CH equation as

$$\mathcal{F} = \mathcal{F}_0 \int_{\Omega} d\vec{x} \left\{ \frac{\psi}{2} \left[\varepsilon + \left(1 + \frac{\partial^2}{\partial x^2} \right)^2 \right] \psi - \frac{u}{4} \psi^4 + \frac{1}{6} \psi^6 \right\} \quad (4)$$

and

$$\frac{\partial \psi}{\partial \tau} = \nabla^2 \left\{ \left[\varepsilon + \left(1 + \frac{\partial^2}{\partial x^2} \right)^2 \right] \psi - u \psi^3 + \psi^5 \right\} + \zeta \quad (5)$$

Now we have only three independent parameters: \mathcal{F}_0 , ε , and u . \mathcal{F}_0 has the dimension of energy and the other two are dimensionless. They can be expressed in terms of original parameters: $\mathcal{F}_0 = \lambda q_0^4 / \sqrt{u_6}$, $\varepsilon = a(T - T_L) / q_0^4 = \alpha(T / T_L - 1)$, and $u = u_4 / (q_0^2 \sqrt{u_6})$.

The new random variable ζ whose average value is also zero is subject to the two-point correlation function

$$\langle \zeta(\vec{x}, \tau) \zeta(\vec{x}', \tau') \rangle = D \nabla^2 \delta(\vec{x} - \vec{x}') \delta(\tau - \tau') \quad (6)$$

with $D = k_B T / \mathcal{F}_0$. The average value of $\psi(x, y)$, $\bar{\psi}$, is conserved by Eq. (5) and therefore $\bar{\psi}$ can be taken as an independent parameter.

3. Main simulated results and analysis

We solve the dimensionless evolution equation Eq. (5) by difference method. The Laplace operator ∇^2 and the second-order differential operator $\partial^2/\partial x^2$ are discretized by the central difference formula as usual, and the time coordinate is discretized using the first-order finite differential approximation. The periodic boundary condition is adopted for all the simulations. The initial condition is subject to Gaussian random fluctuations. We find that resultant equilibrium patterns are independent of the random variable ζ . We keep $\bar{\psi} = 0$ because the high-temperature 1×1 phase has $\psi = 0$. The parameter \mathcal{F}_0 is not directly relevant in our solving Eq. (5). We have tried various values for the system sizes and the parameters u and ε . We choose approximately 40 periods or 80 surface lattice constants when doing the main simulations, but confirm our results using larger systems. We use $\delta x = \pi/16$ and $\delta \tau = 10^{-6}$ for the space and time increments. The morphology presented in the following is only a part of the whole system.

Presented in Fig. 2 is the periodic morphology of phase-field-crystal variable $\psi(x, y)$ with the parameters: $u = 0.1$, $\varepsilon = -0.005$, and $\bar{\psi} = 0$. The period is equivalent to 2π within an error of 10^{-5} . The center of the white stripe corresponds the maximum ψ_{\max} and that of the black stripe the minimum ψ_{\min} . This phase-field-crystal simulated dimerization pattern is in agreement with experimental STM images of high-quality Si(001) and Ge(001) dimerized surfaces [2, 3, 4, 5]. This stripe pattern is obtained for the parameter region: $0.00221 > \varepsilon > -0.01$.

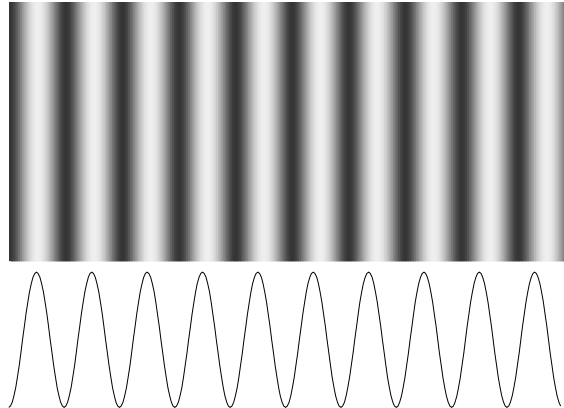


Figure 2. Simulated striped morphology of phase-field-crystal variable ψ (upper part) and its side view curve (lower part). We use the parameters $\delta x = \pi/16$, $\delta \tau = 10^{-6}$, $u = 0.1$, $\varepsilon = -0.005$, and $\bar{\psi} = 0$.

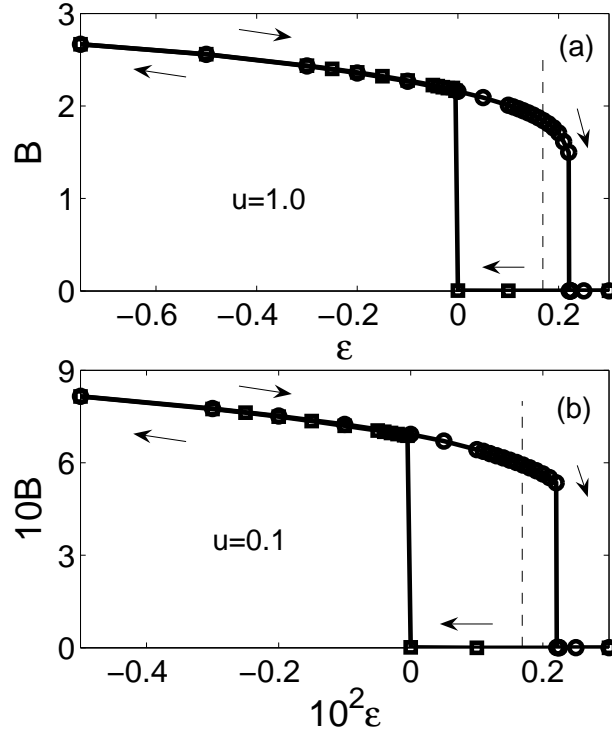


Figure 3. The calculated parameter B as a function of $\varepsilon = a(T - T_L)$, with the phase-transition point ε_c indicated by dash line. The ε -increasing part is shown by the solid line with circles, and the ε -decreasing part by the solid line with squares. The phase coexistence region is defined by $\varepsilon_L \leq \varepsilon \leq \varepsilon_H$. The parameter set $(\varepsilon_L, \varepsilon_c, \varepsilon_H)$, corresponding to (T_L, T_c, T_H) , is $(0.0, 0.169, 0.221)$ for $u=1.0$, and $(0.0, 0.00169, 0.00221)$ for $u=0.1$.

We use $B = \psi_{\max} - \psi_{\min}$ as our order parameter and present its ε dependence for $u=1.0$ and $u=0.1$ in Fig. 3. It is clear that the phase transition is of first order. The B , as a function of ε , in the case of $u = 0.1$ is ten times smaller than that in the case of $u = 1.0$. The ε width of the phase coexistence region, $\varepsilon_H - \varepsilon_L$, is proportional to u^2 . Because ε is proportional to $T - T_L$, the ε dependence implies the temperature dependence from zero temperature to T_L , and finally beyond T_H . It is proved using a series of simulated results that T_c is also proportional to u^2 . Therefore, the parameter u describes the temperature width of phase coexistence region. Systematical analysis of simulated results shows that ψ can be quantitatively described by the function

$$\psi = \frac{B}{2} \sin\left(\frac{q}{q_0}x\right), \quad (7)$$

especially in the neighborhood of the maximum and the minimum. Here B and q are determined by the simulated results. $|q/q_0 - 1|$ can be very small as long as u is small enough. Actually, q is equivalent to q_0 within a tiny error less than 10^{-5} as long as u is smaller than 0.1.

On the other hand, B and q can be analytically determined by minimizing the free

energy (4) in terms of a variational expression $\psi = C \sin(px)$ similar to Eq. (7). In this way, we derive $p = 1$ and

$$C = \frac{1}{\sqrt{5}} \sqrt{3u + \sqrt{9u^2 - 40\alpha(T/T_L - 1)}}. \quad (8)$$

This means $q = q_0$. The expression (8) is reasonable only when T is not larger than T_H , which implies that u can be expressed as

$$u = \frac{2}{3} \sqrt{10\alpha(T_H - T_L)/T_L}. \quad (9)$$

We can obtain an analytical expression of the order parameter $B = 2C$ for $u \leq 0.1$ by requiring that C given by Eq. (8) is equivalent to $B/2$ obtained by numerically solving Eq. (5). The phase-transition temperature T_c is given by

$$T_c = \frac{3}{4}T_H + \frac{1}{4}T_L. \quad (10)$$

Using the relation $\phi = q_0\psi$ (due to $u_6 = 1$) and Eq. (9), we obtain $B = \Delta b/c$ and

$$\Delta b = 2c^4 \sqrt{\frac{8\alpha(T_H - T_L)}{5T_L}} \sqrt{1 + \sqrt{\frac{T_H - T}{T_H - T_L}}} \quad (11)$$

for $T \leq T_H$, and $B = \Delta b = 0$ for $T > T_H$. This expression determines the temperature dependence of the dimerization-induced change of the bond length, Δb .

4. Applied to the (2×1)-(1×1) phase transitions of Si(001) and Ge(001)

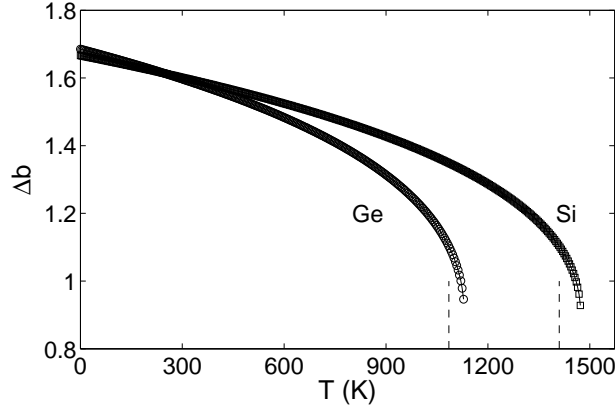
For the Si(001) and Ge(001) dimerized surfaces, it is relatively easy to measure T_L , T_H , c_0 (zero temperature), and Δb_{RT} (room temperature, 300 K). It should be noticed that $q = 2\pi/\bar{c}$, where $\bar{c} = 2c$ ($\bar{c}_0 = 2c_0$). We use these parameters as input. The parameter α can be determined by substituting 300 K and Δb_{RT} for T and Δb in Eq. (11), and then calculate u and T_c in terms of Eqs. (9) and (10). We calculate u_4 using the definition $u_4 = uq_0^2$ (due to $u_6 = 1$). The input and calculated results are summarized in Table I. In Fig. 4 we present the dimerization parameter Δb as a function of temperature for both the Si(001) and the Ge(001) surfaces. It is clear that Δb is still finite at T_c , and jumps to zero once T is larger than T_H .

It should be pointed out that our phase-field-crystal equilibrium patterns, as shown in Fig. 2, consist of regular arrays of infinitely long dimer chains. These are in agreement with large-scale experimental STM images of the parallel perfect dimer chains in the high-quality Si(001) and Ge(001) surfaces [4, 5]. Generally speaking, such a dimer chain can be broken into several segments, but these segments are still completely in the same line [4, 5, 2, 3, 6, 7] and can be considered to be an infinitely long dimer chain in the sense of averaging along the line. Actually, there is either type- S_A or type- S_B dimerized phases in high-quality (001) surfaces [4, 5]. Therefore, our phase-field-crystal theory can describe well the experimental regular arrays of dimer chains.

In addition, our simulated results are in agreement with experimental observation that the dimers still exist above T_c [6], as shown in Fig. 4. Some of the dimers begin

Table 1. The input parameters and the calculated results for the dimerized Si(001) and Ge(001) surfaces.

Si(001)	T_L (K)	T_H (K)	c_0 (Å)	Δb_{RT} (Å)
	1223	1473	3.84	1.6
	α	u	u_4	T_c (K)
	5.8×10^{-4}	0.022	0.06	1410
Ge(001)	T_L (K)	T_H (K)	c_0 (Å)	Δb_{RT} (Å)
	950	1130	3.99	1.6
	α	u	u_4	T_c (K)
	5.4×10^{-4}	0.020	0.05	1085

**Figure 4.** The temperature dependences of dimerization parameter Δb (Å) for the Si(001) (square) and Ge(001) (circle) phases, with T_c indicated by dash line. T_H is 1473 K for the Si(001) and 1130 K for the Ge(001). Δb is finite at T_c , and jumps to zero once $T > T_H$.

to break at T_L and all of them finally disappear at T_H . Between T_L and T_H , there is a phase coexistence of the normal dimers and the broken ones, but there is no coexistence of the type- S_A and type- S_B discussed in earlier references [25]. This is the clear sign of the first-order phase transition and thus there must be some dimers above the phase transition temperature T_c . Naturally, $T_H - T_c$ varies in different samples, and can be so small that T_H is equivalent to T_c within measurement error, which leads to some conclusions that there is no dimers above T_c [7]. Essentially, a structural phase can be judged only when it has a large enough spatial size. Therefore, our modeling and simulated results are not only reasonable but also in agreement with experiment [6, 7].

5. Conclusion

In summary, we have proposed a two-dimensional phase-field-crystal model for the Si(001) and Ge(001) dimerized surface phases and their phase transitions to

corresponding 1×1 phases at elevated temperatures. We use a phase-field-crystal variable to describe the dimerization of atoms in the top layer, and determine it by solving the evolution equation derived from the free energy. The simulated periodic arrays of dimer chains are consistent with STM images of the Si(001) and Ge(001) dimerized surfaces. The calculated temperature dependence of the dimerization parameter shows that normal dimers and broken ones coexist between T_L and T_H and the first-order structural phase transition takes place at T_c in between. These results are in agreement with experiment. This phase-field-crystal approach can be directly applied to phase transitions of semiconductor $n \times 1$ reconstructed surface phases, and should be suitable to other semiconductor reconstructed surfaces and their phase transitions.

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